

## THERMAL AND KINETIC STUDY OF THE MILD PYROLYSIS OF SINGLE SUBBITUMINOUS COAL PARTICLES

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### INTRODUCTION

A detailed knowledge of coal pyrolysis is fundamental to the understanding of the early stages of many coal conversion processes. Pyrolysis studies have been conducted using a variety of techniques including the use of electric grids (1-3), thermogravimetric analyzers (4-6), entrained flow reactors (7-9), and fluidized beds (10,22). In order to eliminate the complexity introduced by particle interactions, some research has been directed towards the behavior of single coal particles (12-16). For example, Huang et al. (12) measured the transient temperature gradients in the gas surrounding a captive 1 mm diameter coal particle with a fast response thermocouple array (12) and found steep gradients up to 4 mm from the surface. Saito et al. (16) reported on differences between high temperature devolatilization in air and N<sub>2</sub> for 2-4 mm-sized particles, and conducted an isothermal kinetic analysis of the data. Hertzburg (17) analyzed experimental data from laser-heated coal pyrolysis experiments and concluded that the pyrolysis rate was controlled by the heat flux to the particle surface and by thermodynamic transport constraints within the particle. He proposed a "rate coefficient", which is the reciprocal of the overall enthalpy required for heating and devolatilization. The significance of heat transfer effects on coal pyrolysis were recently reviewed by Suuberg (18) and Gavalas (19), and it is clear that heat transfer plays an important role. Nevertheless, few references can be found in the literature on the instantaneous rate of heat transfer to pyrolyzing coal particles. Most measurements in this area have been made using Differential Scanning Calorimetry (DSC) which is limited to low heat fluxes during the heatup to pyrolysis temperature. The current work is an attempt to relate experimentally measured particle temperature and mild pyrolysis rates in order to determine meaningful kinetic parameters.

### EXPERIMENTAL

#### Temperature Measurements

Pyrolysis experiments on 1 mm diameter coal particles were performed in a captive reactor, details of which have been provided elsewhere (12,13). It consists essentially of two enclosing horizontal tube furnaces which are heated electrically to preheat the incoming gas and maintain the reactor at a predetermined temperature. A subbituminous coal (volatile matter 50.5%, fixed carbon 36.0%, ash 13.5%) was used in this study. Prepurified nitrogen was used to purge air from the reactor but prior to the start of a run, the gas flow was stopped so that the experiments were essentially in a static system. For each run a 1 mm diameter coal particle was injected into a minicrucible inside the 873 K reactor. Temperature gradients in gas surrounding the reacting particle were measured by a thermocouple array (TCA) composed of four extra-fine thermocouples spaced 1.0 mm apart. The distance from the coal particle surface to the closest thermocouple was approximately 1 mm. A microcomputer collected the responses of the thermocouples at millisecond time intervals.

All experiments were conducted on dry coal particles, the coal being dried overnight at 383°K in a vacuum oven prior to use. A char particle was prepared by injecting a coal particle into the reactor in flowing nitrogen at 873 K for 5 minutes.

#### Measurements of Weight Loss

Weight loss data for pyrolysis were obtained in a Dupont 951 Thermogravimetric Analyzer (TGA). To simulate the process of dropping a cold coal particle into a hot reactor, the TGA quartz tube was kept in the furnace during heatup in a 75 cc/min flow of prepurified nitrogen. The sample housing was then rapidly introduced into the hot quartz tube in the furnace after the furnace temperature had

stabilized (20,21). The same experimental conditions were used in the TCA and TGA experiments (temperature, particle size, etc.).

## RESULTS AND DISCUSSION

### Heat Transfer

The temperature histories measured by the TCA in the surrounding gas at different distances from the coal particle surface during pyrolysis are shown in Figure 1. Curves 1 to 4 express instantaneous temperatures at 1, 2, 3, and 4 mm from the particle surface, respectively. Because of thermal continuity in the gas surrounding the pyrolyzing coal particle, the measured data were extrapolated to the particle surface by a three order polynomial correlation in order to obtain the instantaneous particle surface temperature (Figure 2). The extrapolated surface temperature ( $T_s$ ) is plotted as curve 0 in Figure 1. The temperature of the gas phase 5 mm from the particle was taken to be the furnace temperature ( $T_f$ ) in the extrapolation. The validity of this assumption is based on solid evidence. Firstly, as heat was transferred to the vicinity of a cold coal particle, the temperature of the surrounding gas recovered to, but did not exceed, the furnace temperature (12). Secondly, the temperature perturbation decreased with distance from the particle surface. Figure 2 provides information on spatial temperature gradients, from which heat transfer boundary conditions were determined. Under the experimental conditions, the boundary was a spherical region with a radius of approximately 5 mm.

The three order polynomial used in the extrapolation is expressed as:

$$T = A_0 + A_1X + A_2X^2 + A_3X^3 \quad 1)$$

where  $A_i$  ( $i = 0, 1, 2, 3$ ) is constant at a given time  $t$ ,  $X$  is the dimensionless distance expressed by:

$$X = \frac{x}{x_b} \quad 0 \leq X \leq 1 \quad 2)$$

in which  $x$  is the distance from the particle surface and  $x_b$  is the distance from the particle surface to the heat transfer boundary. From Equation (1)  $T_s$  can be determined by:

$$T_s = T|_{x=0} = A_0 \quad 3)$$

and bulk gas temperature can be expressed as:

$$T_f = T|_{X=1} = \sum_{i=0}^3 A_i \quad 4)$$

Figure 3 shows temperature histories for char particles under the same experimental conditions as for the coal particles in Figure 1. The char particles were recovered from the preceding coal run. Since the coal used in this study is non-swelling (free swelling index = 0) the particle size and external surface areas of the coal and char particles were considered to be the same.

Particle surface temperatures for the coal and char are plotted in Figure 4. During the early stage of heatup to 700 K (up to ~2s)  $T_s$  for the coal was about 80 K lower than  $T_s$  for the char. This is due to the initial mass difference between the coal and char particles. At the onset of pyrolysis for the coal, there was an inflection in the  $T_s$  curve. Endothermic pyrolysis reactions kept the coal particles at a lower temperature than the char which was undergoing a rapid heatup to the furnace temperature. The unambiguous surface temperature histories in Figure 4 indicate that there will be a gross error if the particle surface temperature is assumed to be the furnace temperature.

Heat flux by radiation from the furnace wall to the coal and char particles can be calculated from the following equation:

$$q_R' = \epsilon \sigma (T_f^4 - T_s^4) \quad 5)$$

To estimate maximum radiation, the emissivity  $\epsilon$  of coal and char is assumed to be unity. The rate of heat transfer by conduction from the hot surrounding gas can be expressed as:

$$q_c = K \bar{A} \frac{\Delta T}{\Delta x} = K \bar{A} \frac{(T_f - T_s)}{(d_b - d_s)} \quad 6)$$

where

$$\bar{A} = \frac{A_b - A_s}{\ln \left( \frac{A_b}{A_s} \right)} = \frac{\pi (d_b^2 - d_s^2)}{2 \ln \left( \frac{d_b}{d_s} \right)} \quad 7)$$

Assuming the coal and char are surrounded by nitrogen, the thermal conductivity of nitrogen can be used in the calculation. The heat flux due to conduction to the coal and char particles can be estimated by:

$$q_c' = q_c / A_s \quad 8)$$

The heat transfer coefficient for convection is determined from the Nusselt number (taken as two) (22) and the diameter of the particle,  $d_s$ , by:

$$h = Nu K d_s \quad 9)$$

where  $K$  is the thermal conductivity of the surrounding gas. The heat flux to the particle by convection can be determined by:

$$q_v' = h(T_f - T_s) \quad 10)$$

The heat fluxes due to radiation, conduction, and convection as function of the time are shown in Figures 5 and 6 for coal and char particles, respectively. The instantaneous heat fluxes are a strong function of the residence time. The total heat fluxes varied from 27 w/cm<sup>2</sup> at the beginning to zero at the end of a run corresponding to a 9 s time interval. The dominant mode of heat transfer was conduction. Radiation contributed less than convection in the early heat up stage. However, after 2 s the same amount of heat was supplied by radiation as supplied by convection.

A comparison of the total heat flux to the coal and char particles is shown in Figure 7. The smooth decay in heat flux for both the char and coal in the early stage (< 2s) characterizes the heatup processes. An obvious inflection occurs in the heat flux curve for the coal, which implies the initiation of pyrolysis. More heat is received by the coal than the char to meet the needs of endothermic pyrolysis until the coal is converted into char. The total heat required to heat and pyrolyze the coal particles can be calculated by integrating the heat flux:

$$Q = \frac{A_s}{W_d} \int_0^\infty q_t' dt = \frac{A_s}{W_d} [\Sigma (q_c' + q_v' + q_R') \Delta t] \quad 11)$$

where  $W_d$  is the sample weight on a dry basis. The calculated heats required by the coal and char are shown in Figures 8 and 9, respectively. The figures show clearly that the heat transferred through the

surrounding gas by conduction and convection amounts to 80% of the total. Only 20% of the heat is contributed by radiation. This is not surprising since heat transfer by conduction and convection is proportional to the temperature difference,  $\Delta T = T_f - T_s$ , whereas the driving force for radiation is proportional to the difference between the fourth powers of the temperatures,  $T_f^4 - T_s^4$ , a much stronger function of the absolute furnace temperature. Therefore, at higher  $T_f$ , radiation plays a more important role. From Eq. (11) the total heat needed to heat the char to 873 K is 1917 J/g. The heat required to heat coal and pyrolyze it is 2219 J/g (dry basis). Assuming that the original coal, char and volatiles have the same specific heats, about 300 J/g is needed for the decomposition. This is less than 15% of the total heat required by the coal. Therefore, the heat capacity is the major term in the heat transfer calculation.

### Kinetics

Devolatilization results from the TGA experiments are presented in Figure 10. The data are expressed as the percentage weight loss of the coal (daf) versus residence time. The particle surface temperature for the same size coal particles at the same furnace temperature as for the TGA method is also plotted in Figure 10. The inflection point A on the  $T_s$  curve is the pyrolysis initiation point, as discussed before, and the completion point B is defined as the time when  $T_s$  equals  $T_f$ . The weight loss data are consistent with these temporal characteristics. Before the initiation point, only about 2% weight loss is observed, but up to the completion point more than 95% of the total weight loss is reached. The total weight loss is about 37% (daf) which is less than the ASTM proximate volatile matter (~50%). This is because the experiments were performed at a temperature of more than 300 K less than the ASTM test.

The fact that negligible weight loss was observed before point A proves that two distinct processes occur during pyrolysis, namely heatup and reaction. Badzioch and Hawksley (23) reported negligible weight loss until the coal particles reached about 673 K, before the pyrolysis reaction became significant. They expressed the total pyrolysis time as:

$$\tau T = \tau H + \tau R \quad (12)$$

where the subscripts T, H, and R represent the total, heatup, and reaction times, respectively. For millimeter-sized coal particles, the heatup stage is more significant. Under the conditions in this study, for 1 mm particles, it took 2 s to initiate the pyrolysis reaction.

As a first attempt to determine pyrolysis rates for the millimeter-sized single coal particles in the TGA, a simple first order model was used:

$$\frac{dV}{dt} = kV \quad (13)$$

$$\text{where} \quad V = 1 - \frac{W}{W_\infty} \quad (14)$$

$$\text{and} \quad k = k_0 \exp(-E/RT_p) \quad (15)$$

Because of the difficulty of measuring the particle temperature,  $T_p$ , most kinetic studies use Eq. (13) with the assumption that the coal particle is instantaneously heated to the furnace temperature. This may be allowable for smaller pulverized coal but is not acceptable for millimeter-sized, or larger particles, although it has still been used by others (16). In this study an attempt was made to reduce the error caused by the improper assumption of isothermality. The particle surface temperature,  $T_s$ , is substituted into Eq. (15) for  $T_p$ . This is based on the assumption that the thermal conductivity of the coal is infinite. This is not correct but is an improvement over use of the heat source temperature. Therefore, Eqs. (13) and (15) can be expressed as:

$$\frac{dV}{dt} = k_0 \exp(-E/RT_s) V \quad (16)$$

or:

$$\ln \left( \frac{1}{V} \cdot \frac{dV}{dt} \right) = \ln k_0 - \frac{E}{R} \cdot \frac{1}{T_s} \quad (17)$$

The logarithm term on the left hand side of Eq. (17) is plotted against the reciprocal of  $T_s$  in Figure 11. The activation energy and pre-exponential factor were derived from the slope and the intercept of the straight line in Figure 11. The activation energy estimated from Eq. (17) is 34.0 kcal/mole and the pre-exponential factor is  $4.8 \times 10^8 \text{ s}^{-1}$ . The activation energy is more than four times that reported by Saito et al. (16) for pyrolysis of millimeter-sized subbituminous coal particles.

## CONCLUSIONS

A thermocouple array was used to measure temperature gradients in the gas phase around captive coal and char particles during heatup and pyrolysis in preheated nitrogen. Instantaneous particle surface temperatures were extrapolated from the measured gas temperatures at different distances from the particles. Based on basic heat transfer principles, heat fluxes of conduction, convection, and radiation were calculated. Heat fluxes to the particles were strongly dependent on residence time, varying from 27 W/cm<sup>2</sup> to 0 at the completion of pyrolysis. The total heat required for heatup and pyrolysis was determined by integration. The results indicated that 80% of the total heat was transferred through the gas phase by conduction and convection. Radiation at the low operating temperature made a minor contribution to the total heat transfer.

The temperature history of the 1 mm diameter coal particles indicated that pyrolysis did not occur isothermally. Two seconds elapsed prior to the onset of pyrolysis. Particle surface temperatures were substantially lower than the furnace temperature until pyrolysis was completed.

An attempt was made to use instantaneous particle temperatures in a kinetic analysis. Weight loss data were obtained using a modified TGA method which simulated the TCA conditions. An activation energy and pre-exponential factor were estimated from a first order rate expression the values being 34 kcal/mole and  $4.8 \times 10^{-8} \text{ s}^{-1}$ , respectively.

## ACKNOWLEDGEMENTS

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## NOMENCLATURE

$\bar{A}$	Logarithm average area, cm <sup>2</sup>	$q_V$	Heat flux of convection, W/cm <sup>2</sup>
$A_b$	Area of heat transfer boundary, cm <sup>2</sup>	$R$	Universal gas constant
$A_s$	Area of particle surface, cm <sup>2</sup>	$T_f$	Furnace temperature, K
$d_b$	Heat transfer boundary diameter, cm	$T_p$	Particle temperature, K
$d_s$	Particle diameter, cm	$T_s$	Particle surface temperature, K
$E$	Activation energy, kcal/mole	$t$	Time, s
$h$	Coefficient of convective heat transfer, W/cm <sup>2</sup> K	$t_H$	Heatup time, s
$K$	Thermoconductivity, W/cm K	$t_R$	Reaction time, s
$k$	Rate constant, s <sup>-1</sup>	$t_T$	Total time, s
$k_0$	Pre-exponential factor, s <sup>-1</sup>	$V$	Fraction of remaining volatiles
$Nu$	Nusselt number	$W$	Weight loss at time $t$
$Q$	Total heat, J	$W_d$	Sample weight on dry basis, g
$q_c$	Heat transfer rate by conduction, W	$W_\infty$	Maximum weight loss, g
$q_c$	Heat flux by conduction, W/cm <sup>2</sup>	$X$	Dimensionless distance
$q_R$	Heat flux by radiation, W/cm <sup>2</sup>	$x$	Distance, cm
$q_T$	Total heat flux, W/cm <sup>2</sup>	$x_b$	Distance from particle surface to heat transfer boundary, cm
		$\epsilon$	Emissivity
		$\sigma$	Stefan-Boltzmann Constant

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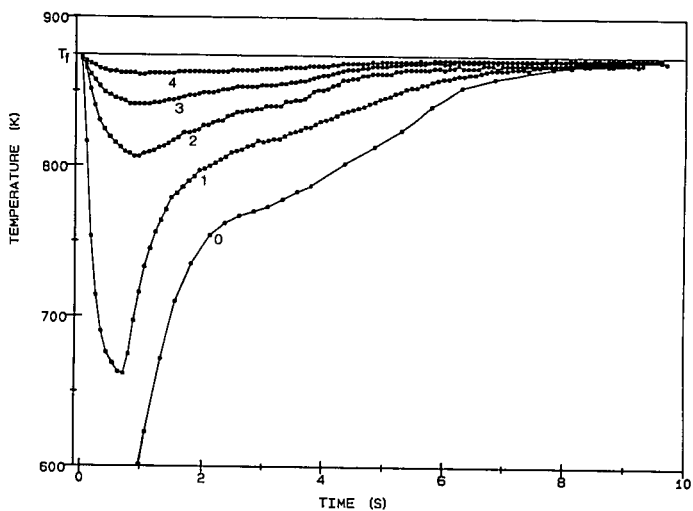


Figure 1. Gas Phase Temperature (0-4 mm From Particle Surface) During Pyrolysis of a 1 mm Diameter Coal Particle at 873 K

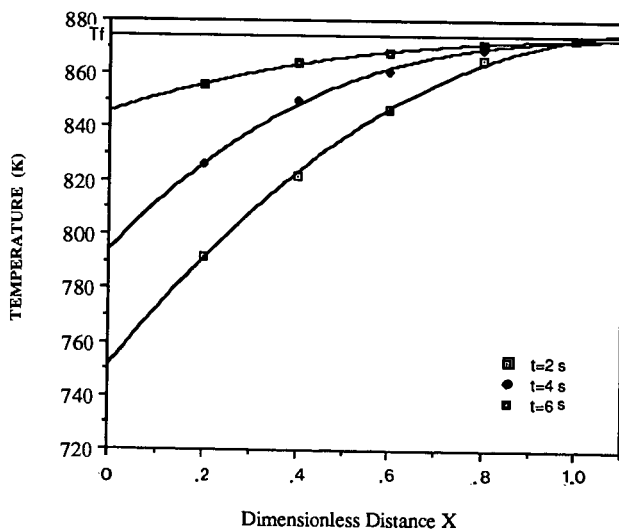


Figure 2. Extrapolation of Data from Figure 1 to Predict Surface Temperature

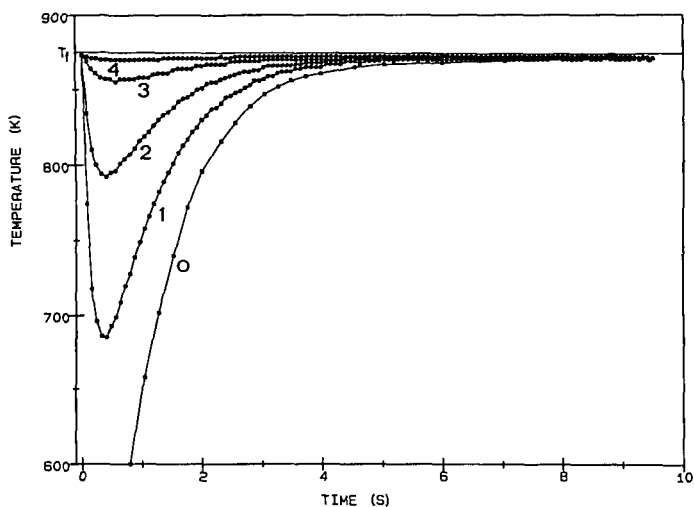


Figure 3. Gas Phase Temperature (0-4 mm From Particle Surface) During Heatup of a 1 mm Diameter Char Particle at 873 K

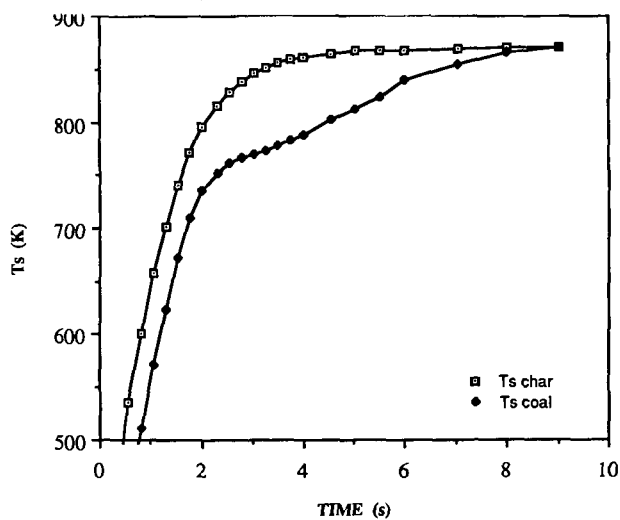


Figure 4. A Comparison Between Coal And Char Surface Temperatures as a Function of Time During Heating in Nitrogen at a Furnace Temperature of 873 K



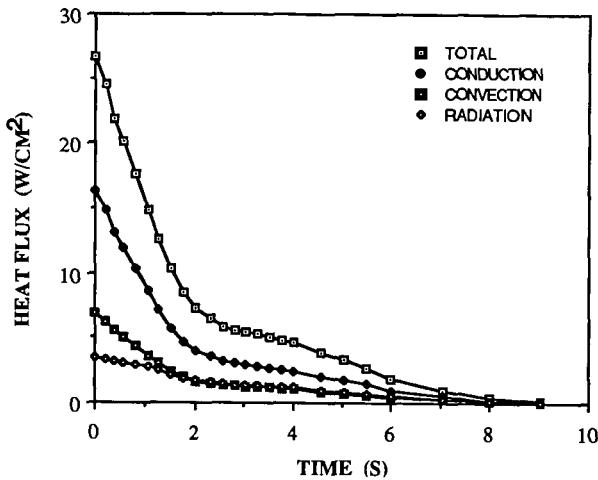


Figure 5. Time Dependency of the Contribution of Conductive, Convective and Radiative Heat Fluxes to the Total Heat Flux to a 1 mm Diameter Coal Particle Heated in Nitrogen at a Furnace Temperature of 873 K

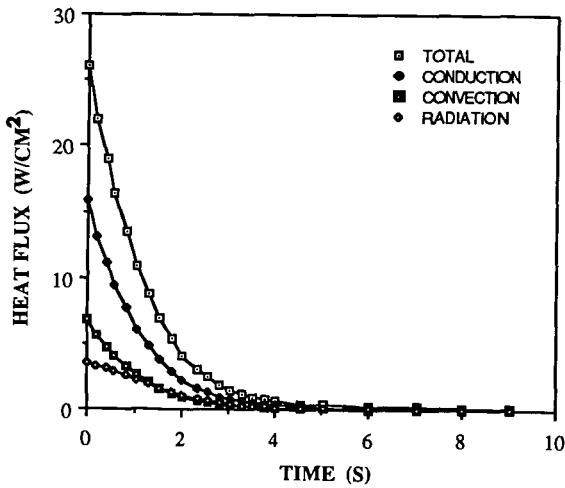
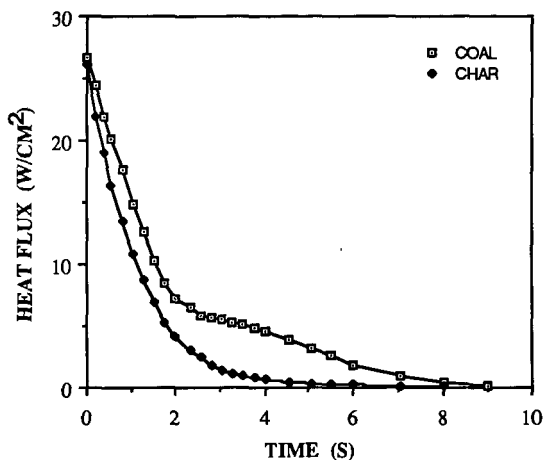
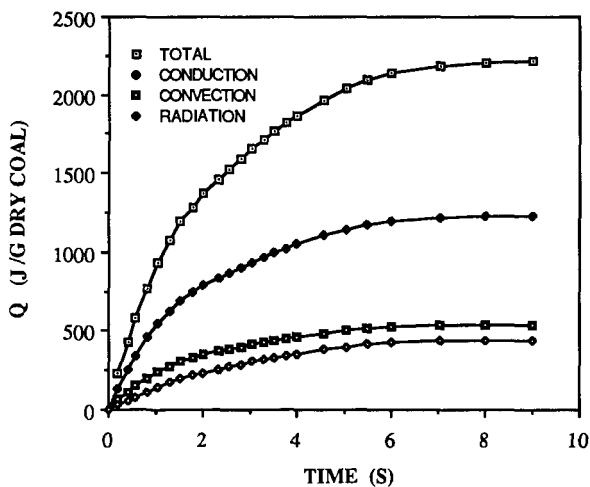


Figure 6. Time Dependency of the Contribution of Conductive, Convective and Radiative Heat Fluxes to the Total Heat Flux to a 1 mm Diameter Char Particle Heated in Nitrogen at a Furnace Temperature of 873 K



**Figure 7. Comparison Between Total Heat Flux to 1 mm Diameter Coal and Char Particles Heated in Nitrogen at 873 K as a Function of Time**



**Figure 8. Heat Absorbed by a 1 mm Diameter Coal Particle Heated in Nitrogen at 873 K as a Function of Time**

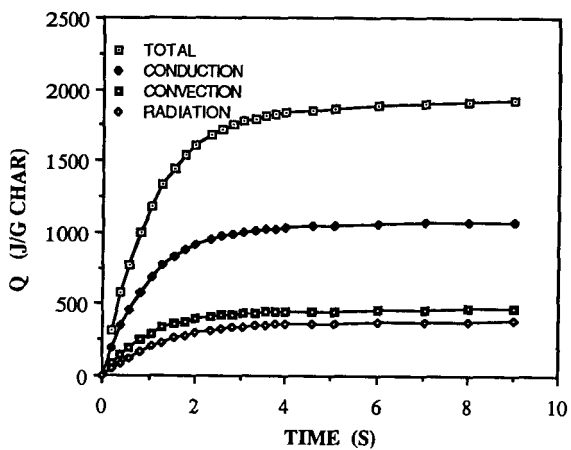


Figure 9. Heat Absorbed by 1 mm Diameter Char Particles Heated in Nitrogen at 873 K as a Function of Time

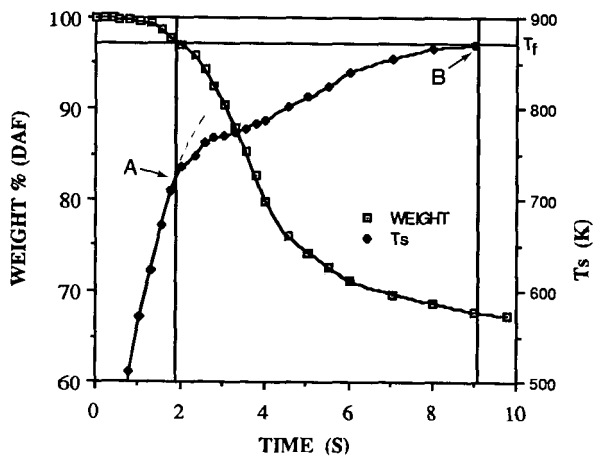


Figure 10. Weight Loss and Surface Temperature as a Function of Time for 1 mm Diameter Coal Particles Heated in Nitrogen at a Furnace Temperature of 873 K

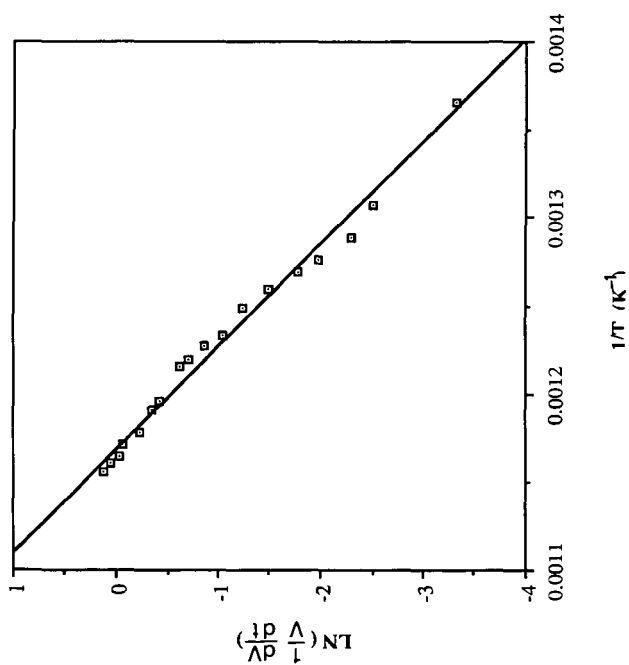


Figure 11. Arrhenius Plot for the Pyrolysis of 1 mm Diameter Coal Particles in  $N_2$  at a Furnace Temperature of 873K